EXPERIMENTAL OBSERVATIONS OF DEFORMATION MECHANISMS IN METALLIC NANOLAMINATES

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Abstract

A series of experiments have been performed to examine the deformation and fracture mechanisms that operate in metallic nanolaminated systems. A brief review is made of theoretical and experimental work to date on nanolaminated materials. TEM observations from the present study in deformed materials as well as observations from *in situ* TEM deformation experiments have confirmed the presence of several theoretically postulated deformation mechanisms. These include the generation and motion of 'Orowan' bows, an apparent Koehler image force strengthening effect, and direct observation of the effect of interfaces on the motion and arrangement of dislocations.

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Introduction

Nanolayered materials are being increasingly studied for their interesting mechanical properties and high strength-to-weight ratio. It has been found experimentally that the hardness and ultimate tensile strength of nanolayered structures increases with decreasing bi-layer thickness, in a relation analogous to Hall-Petch behavior to some critical layer thickness. At smaller wavelengths, the hardness is seen to increase more rapidly, with Hall-Petch exponents on the order of unity or greater, to some peak stress value that is much greater than that attainable by traditional microstructures. The deformation mechanisms that operate in these structures have not been experimentally studied extensively, but have been the subject of theoretical analysis. A recent review article details the various models and experimental studies performed on nanolayered materials (1).

The strengthening mechanisms fall into several broad categories. The first is the classic Hall-Petch (2,3) mechanism, where the strength of the microstructure is related to the stress at the head of dislocation pileups initiating slip in adjacent grains. This sort of analysis predicts an inverse square root dependence of the flow stress (or by analogy, the hardness and ultimate tensile strength) on the layer thickness in the nanolaminate. As mentioned above, this sort of behavior seems to dominate at larger wavelengths, where the structures are thought to be able to form pileups. Another mechanism was initially described by Koehler (4), where the image forces imposed by the layers of alternating materials restrict the motion of dislocations. The dislocations are attracted to the lower modulus material, and accumulate within that layer if transmission across the interface is possible, pileup along the interface if transmission is not possible. Koehler predicted an inverse first power relationship between hardness and layer thickness, which was reportedly experimentally confirmed by Lehoczky (5). Another deformation mechanism involves the formation and propagation of so-called 'Orowan' bows within the layer (6). These are dislocations that span the layer and terminate on an interfacial dislocation being laid down on each bounding interface. Again, this analysis predicts an inverse first power relationship between hardness and the layer thickness. Finally, a model proposed by Xu and Barnett (7) shows the influence of interfacial stress on the hardness, and this effect was observed by examining the effect of varying misfit in a series of epitaxial nitride superlattices on the observed hardness.

It is difficult to examine the models developed to date using the experimental results found in the literature because of the complex as-processed microstructures of the materials in these studies. In most work performed to date, the microstructure of the nanolaminate is unknown, aside from the periodicity of the layering. In many cases, the reported processing techniques and conditions are known to produce complex microstructures, such as nanocrystalline columnar grains. This in-plane microstructure can, in many cases, exert an influence on the mechanical properties that far exceeds the influence of the artificial layering. The models developed to date all treat perfect in-plane crystal structures without boundaries except those of the bi-material interfaces. In many cases, it may be fortuitous that the experiments confirm the theoretical predictions, as the observation is likely due to a complex combination of many factors: layering, modulus mismatch, residual stress, in-plane microstructure, and the peculiarities of the mechanical test being performed. This last point may include the influence of the substrate and the difficulty of quantification of hardness tests and the lack of constraint during tensile tests of free-standing foil samples.

The present study attempts to observe the strengthening mechanisms that operate in nanolayered materials in such a way that the results can be more directly compared to theoretical treatments. To this end, single crystal Cu/Ni nanolaminates formed by electrodeposition on Cu single crystal substrates were used in a series of deformation experiments, and transmission electron microscopy (TEM) was used to observe dislocation arrangements and, in the case of in situ deformation experiments, dislocation generation and motion within a nanolaminate system.

Experimental Procedure

Single crystal Cu/Ni nanolaminates were electrochemically deposited onto electropolished Cu single crystal substrates using a method developed by Moffat (8), which is a modification of a technique developed by Verma and Wilman, (9). Various wavelengths of material were fabricated for the different experiments, and the ratio of layer thickness was at least 2 Ni : 1 Cu, this done to aid in the identification of the constituent layers in the TEM. Some of the material (2 nm Cu / 40 nm Ni) was deformed in compression to introduce dislocations into the structure. Some material was left undeformed for in situ TEM deformation experiments. All samples were overplated with Cu and sectioned and thinned to create cross-sectional TEM samples using jet electropolishing and a GATAN PIPS ion mill.[1] The samples suitable for in situ straining were formed by gluing cross-sectional TEM samples of undeformed material to Cu-2Be tensile bars in a method described elsewhere (10). All samples were viewed in a Philips 430 TEM operating at 300 kV, using either a standard double-tilt holder or a single tilt straining holder. Images were recorded using standard film, or a video camera onto a S-VHS VCR in the case of dynamic experiments. Images from the video tape of dynamic events were acquired using a frame-grabbing video card into a Macintosh computer, the images consisting of the average of 8 sequential frames of the videotape. This was done to decrease noise and obtain a fully interleaved image. Subsequent image processing was limited to adjustment of contrast and brightness for optimal micrograph output.

Results and Discussion

Dislocation Arrangements in Rolled Materials

Nanolayered materials consisting of 2 nm Cu / 40 nm Ni were subjected to compressive plastic deformation by rolling. A typical micrograph of the resulting dislocation structure can be seen in figure 1. The region to the right of the figure is relatively free of dislocations, typical of the undeformed material. The features running vertically that appear to be thick interfaces are in fact 2 nm thick layers of Cu. At this wavelength, the interfaces should be mostly coherent and glissile dislocations would be able to cross from one layer to another. To the left of the figure, it is seen that the structure is full of dislocations, some seen to be spanning individual Ni layers. Closer examination of the region adjacent to the Cu layer reveals that many of the dislocations within the Ni layers are aligned along the interface direction and are piled-up against the Cu/Ni interface. The region at the center of the Ni layers is relatively free of these elongated dislocation structures. As detailed by Koehler (4), the image force created by the difference in elastic moduli in Cu and Ni would draw the dislocations

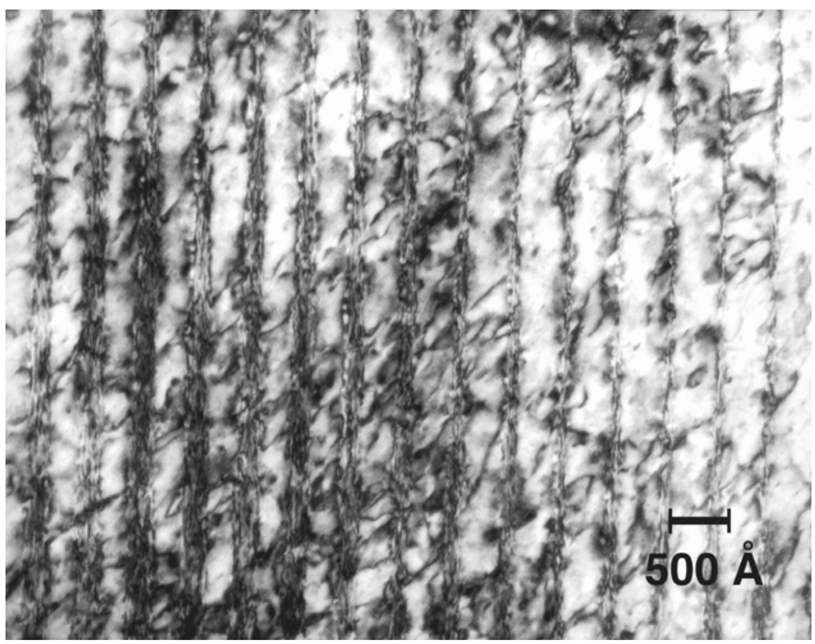

Figure 1: Cross-sectional TEM micrograph of dislocation arrangements in rolled 2 nm Cu / 40 nm Ni electrodeposited nanolaminate.

[1] Identification of sample preparation or imaging equipment by brand name does not imply endorsement by either the National Institute of Standards and Technology nor the United States Government.

to the Cu layer. In this case, it appears that the very small dimension of the Cu layer caused saturation of defects within the layer, and subsequent dislocations piled-up against the interface within the Ni. We interpret this as preliminary evidence of the operation of a Koehler mechanism, though more investigation is indicated with material that is structured such that the Cu layer is thicker and can accommodate more dislocations.

The Effect of Interfaces on Dislocation Motion

It is presumed that the observed large increases in hardness and ultimate tensile strength in nanolaminated materials over conventional microstructures are due to the presence of the interfaces. One of the possible effects is through the interfaces restricting the motion of dislocations from one layer to another. In the case of a completely non-coherent structure, dislocation motion is confined to individual layers. In semi-coherent systems, like Cu/Ni, transmission of dislocations from one layer to another should be possible, as the slip systems line up across the interface. However, the characteristics of the interface will have an effect on dislocation motion. Such characteristics include interfacial sharpness and smoothness, the presence and spacing of interfacial dislocations, and the presence of any intermetallic or impurity species.

We have made two observations that suggest that the interfaces in Cu/Ni single crystal nanolaminates produce a barrier to dislocation transmission, but not an insurmountable one. The first can be seen in figure 2.
Here, a dislocation is seen to span several layers in a 2 nm Cu / 40 nm Ni nanolaminate. Where the dislocation crosses the Ni/Cu/Ni interfaces at the Cu layer, as indicated by the arrows, the lie shape deviates from the smooth bow expected for a dislocation in a crystal of uniform composition. It is seen that the dislocation line forms cusps at the Cu layer intersection, implying that the motion is impeded in the vicinity of the interfaces. It is not clear from this micrograph whether the resistance to motion comes from the interfaces themselves or from the Cu layer, but there is an observable effect.

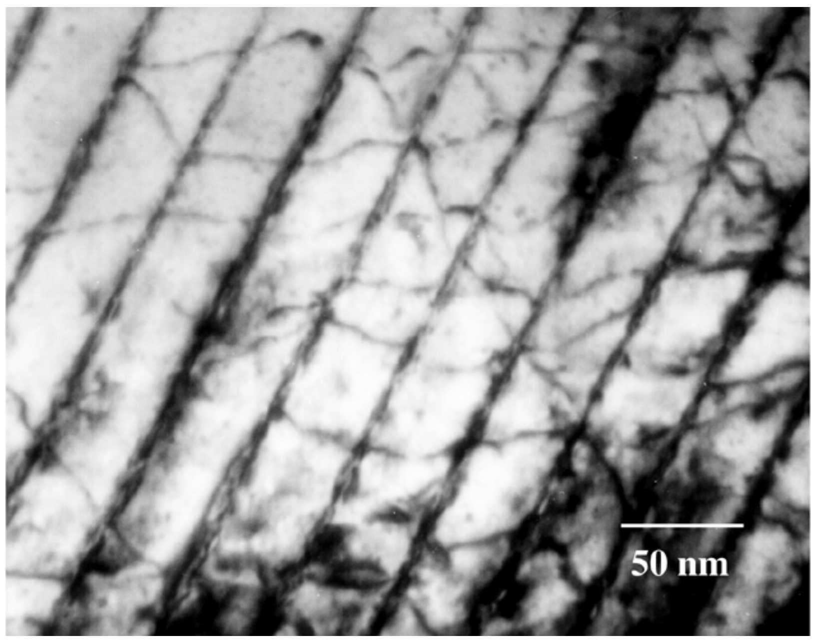

Figure 2: Cross-sectional TEM micrograph of spanning dislocation in rolled 2 nm Cu / 40 nm Ni electrodeposited nanolaminate.

Another observation showing the effect of interfaces on dislocation motion was made during an in situ TEM deformation experiment on a 30 nm Cu / 60 nm Ni nanolaminate sample. In this case, a shear crack nucleated at the edge of the sample and began to emit co-planar screw dislocations into the nanolaminate structure (figure 3). The layered structure consisted of 8 alternating layers on a single crystal (001) Cu substrate. The layers were continuous and could be loaded in tension. As the dislocations encountered the first boundary, they spread laterally within the layer until at least one source nucleated into the next layer from the interface. This source operated, filling this next layer with 'Orowan' bows until another source nucleated in yet the next layer. This behavior can be seen in figure 4. The pileup of 'Orowan' bows can be seen in the layers to the left of the figure, propagating in the direction indicated. At the point indicated by the arrow, a source has nucleated and was seen to operate and fill this layer with dislocations. The pileup was observed to move in this fashion from layer to layer until the interface between the nanolaminate and the substrate was reached, and dislocations were seen to very rapidly generate and saturate the substrate slip plane. The spacing of the dislocations in the pileup within the layers is extremely small, leading to stresses at the head of the pileup that are in the GPa regime. A detailed analysis of the dislocation configurations and stresses in this and other images are the subject of an upcoming paper (11).

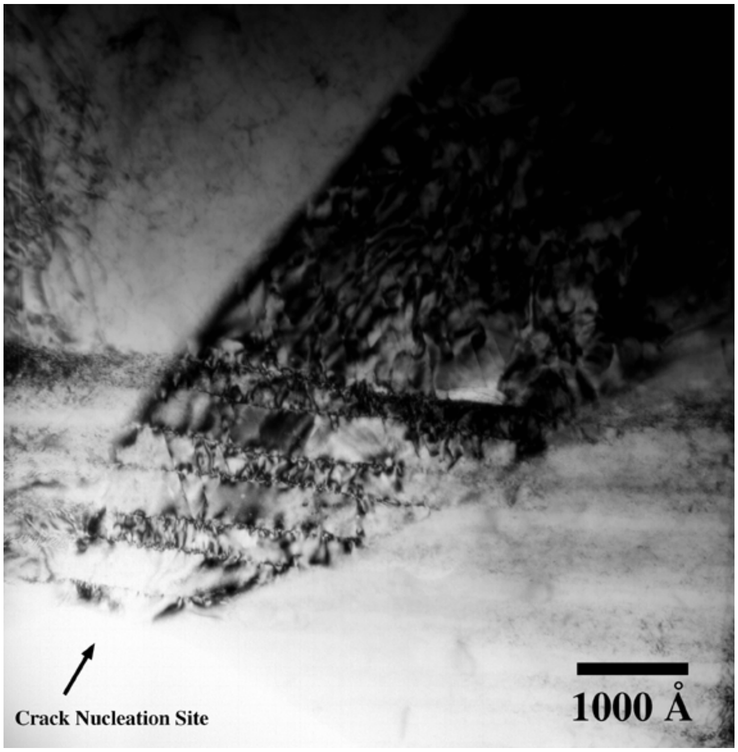

Figure 3: TEM micrograph of in situ strained 30 nm Cu / 60 nm Ni single crystal nanolaminate sample. The tensile direction is parallel to the layers. A shear crack has nucleated, and the active slip plane is defined by the dark contrast region.

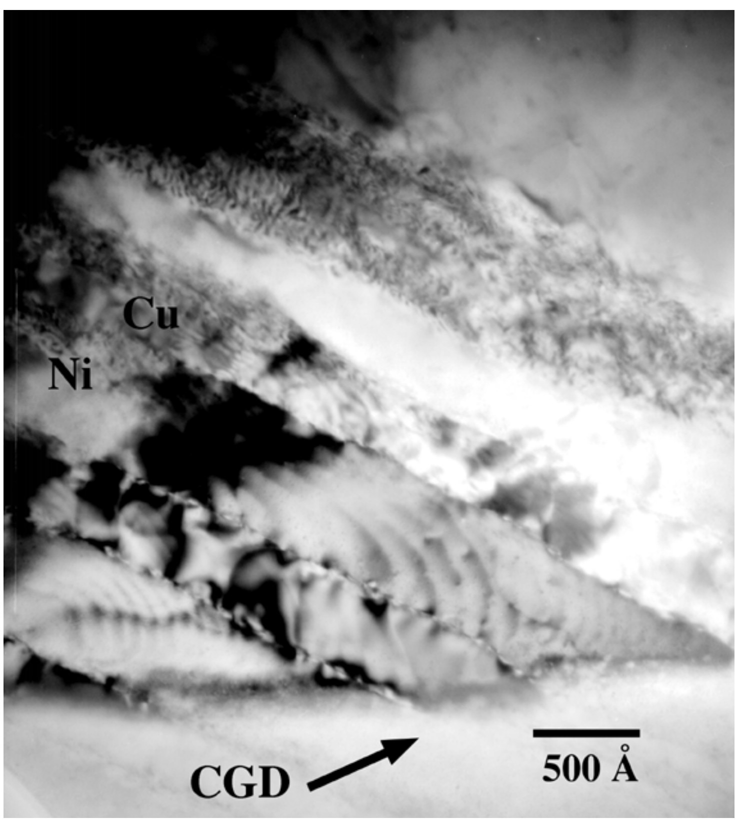

Figure 4: Higher magnification TEM image of pileup emitted from shear crack arranged within the layers of 30 nm Cu / 60 nm Ni single crystal nanolaminate. Small arrow indicates source nucleation into Cu layer. CGD = crack growth direction.

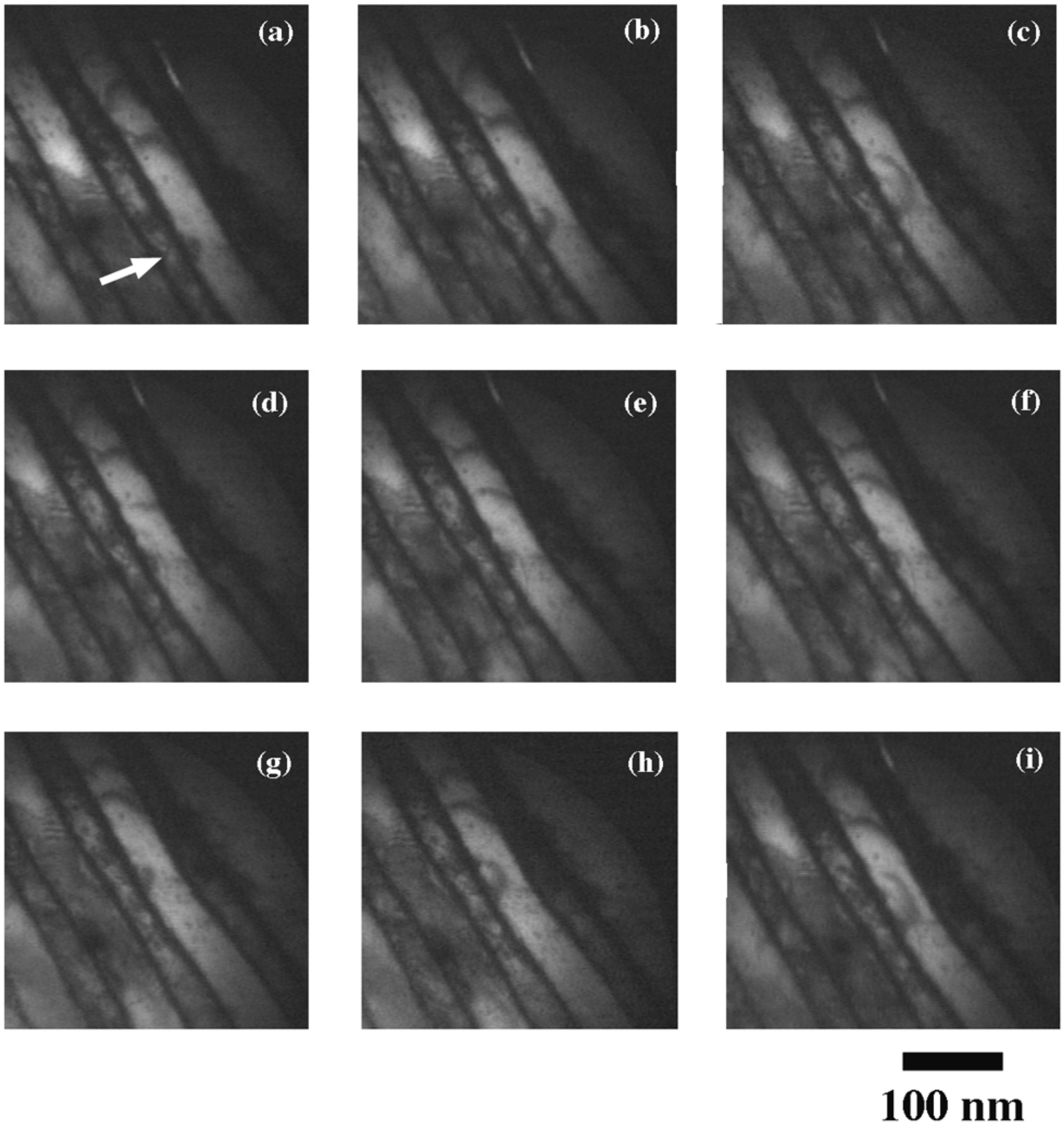

Figure 5: Sequence of images captured from video tape showing the emission of two "Orowan" bows from an interfacial source into a Ni layer in a 30 nm Cu / 60 nm Ni single crystal nanolaminate. The arrow in (a) indicates the source location.

The Generation and Motion of Orowan Bows

A deformation mechanism that has been postulated theoretically for nanolaminates is the formation and motion of ‘Orowan’ bows. The theory (6) predicts an inverse relationship between the strength or hardness and the bi-layer thickness. Evidence of these types of defects have been observed by Hackney and Milligan (12) during straining of a metal/ceramic laminate in the TEM. We have been able to record the generation and motion of ‘Orowan’ bows with individual layers in a Cu/Ni nanolaminate.

A sequence of images showing the emission and motion can be seen in figure 5. All these images are portions of frame-averaged video grabs from the S-VHS recording of the in situ TEM deformation experiment. The arrow in the upper left frame indicates the location of the source in a Ni layer. As one progresses through frames (a) through (i), it is seen that 2 dislocation loops are sequentially emitted into the Ni layer, progress to the next Cu/Ni interface, and join an array of 'Orowan' bows in the layer to the upper left of each frame. It is interesting to note that in all cases when slip progressed from one layer to another in figures 4 and 5, it did so by the nucleation of one or more sources that produced dislocation bows in this fashion.

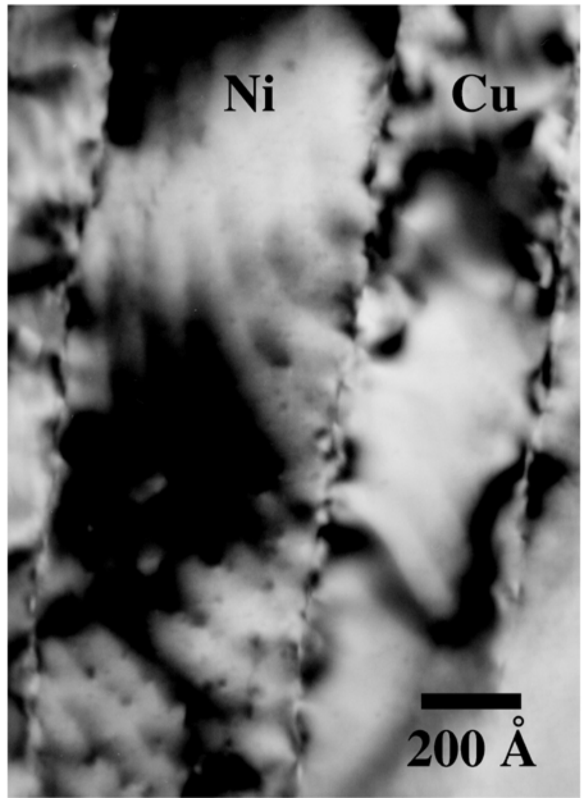

Figure 6: TEM micrograph showing pileup dislocations from Figure 4 pinned on misfit dislocations.

The bows in the pileups within the individual layers generated by this 'Orowan' mechanism are evenly spaced, and are not in the classic pileup configuration. This would indicate that the main resistance to motion of the array is not a single obstacle, but rather a more uniform drag force. The basis of this resistance could be one of several things, but closer examination of the intersections of the pileup dislocations in figure 4 with the interface has given strong evidence of one particular mechanism. As seen in figure 6, the pileup dislcations intersect the interfaces at locations where strong contrast features indicating misfit dislocations are located. The features and intersections are spaced at 5 to 10 nm intervals, which is roughly the misfit dislocation spacing observed in this material at this bi-layer thickness in planview TEM. As the dislocations propagated during the in situ TEM deformation experiment, the motion was seen to be discontinuous and jerky, rather than the smooth advance seen when deforming monolithic single crystal material in the TEM. The advance distances correlated well with the misfit dislocation spacing. It is believed that this is the first direct observation of an operating 'Orowan' deformation mechanism in a structural layered material.

Conclusions

Results have been presented detailing observations of dislocation arrangements, generation and motion in a series of single crystal Cu/Ni nanolaminate samples. The existance of pileups and the generation and motion of 'Orowan' bows have been confirmed, and the observations that suggest the operation of a Koehler hardening mechanism have been presented. It has been seen that the presence of interfaces and misfit dislocations in this semi-coherent structure present a formidable barrier to dislocation motion.

Acknowledgements

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